Potential of thermally integrated high-temperature electrolysis and methanation for the storage of energy by Power-to-Gas

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Abstract

Natural gas is one of the most important primary energy sources with a well developed infrastructure, especially in Europe, and among fossil fuels, natural gas has the lowest CO_2 emissions. It is used in almost all thermal applications in the industry and in domestic, commercial as well as mobile applications.

In addition to the fossil primary energy sources, the share of renewable energies in primary energy consumption is steadily increasing. Amongst others, the share of renewable energy in gross final consumption was 13.0% in 2011 compared with 7.9% in 2004 for the EU27 [1]. However, besides all advantages, this results in a problem caused by the strongly fluctuating electricity supply during the generation by wind power and photovoltaics. An exemplary scenario: If the power supply exceeds significantly the demand, wind power stations have to be switched off and the potential of the systems is not completely utilized. Storage and energy transport technologies are needed providing necessary storage capacity, storage time and transport capacity. Indeed, chemical storages are the only possibility to provide capacities for the case of long-term or seasonal storage.

Especially in Europe, such energy storage is the well developed natural gas infrastructure. The Power-to-Gas-Technology (PtG) is a promising way to transfer electrical excess energy into chemical bond energy like hydrogen or Synthetic Natural Gas (SNG), which can be fed directly into the natural gas grid providing that the gas quality is in compliance with the limit values.

The generation of SNG is realized by coupling electrolysis and methanation. The high-temperature electrolysis offers advantages based on its thermodynamic characteristics compared to conventional electrolysis working at low temperatures. In this way a significant increasing efficiency can be achieved for the reconversion of SNG into heat and electrical power. An example: The efficiency of reconversion SNG generated by PtG with low-temperature electrolysis by Combined Heat and Power (CHP, $\eta \approx 85\%$) is 47%. In case of using PtG with high-temperature electrolysis the efficiency of reconversion increases up to 68%.

High-temperature electrolysis is based on the Solid Oxide Electrolysis Cell (SOEC) technology, which is still at a rather early development state, but shows, due to its thermodynamic characteristics at high temperatures major advantages.

Different variations of coupling HT-electrolysis (700-1000°C) and methanation (200-400°C) are conceivable due to their temperature levels. Amongst others, the heat of reaction of the exothermic methanation can be completely used for the evaporation of the process water for the electrolysis. Co-electrolysis of water and carbon dioxide and recirculation of process flows are further opportunities.

Different possible process schemes for coupling high-temperature electrolysis and methanation are shown in the presentation and are compared with the low-temperature electrolysis case.

1 Power-to-Gas

The increasing amount of electrical energy by renewable energies has a crowding-out effect on conventional power energy. However, a main critical aspect is given by the fluctuating characteristic of the renewables. If supply exceeds power demand, operators of wind power stations will be forced to shut down and the full capacity of the plant is not met. One solution of this suboptimal behavior is a storage- and transport technology that is able to provide required storage capacity as well as storage time and transport capacity. Hereby, conversion into chemical bond energy is the primary solution to meet required capacities in cases of long time and seasonal storage. An interesting way is the technology of Power-to-Gas (PtG), illustrated schematically in figure 1.
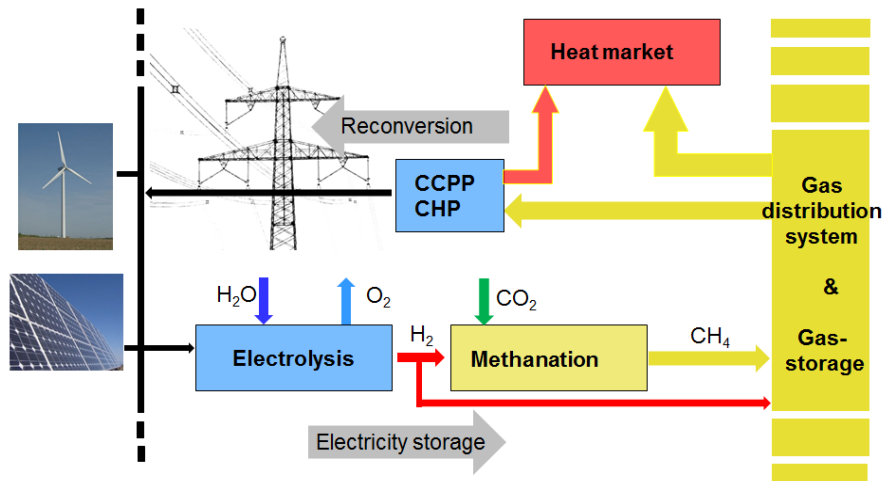

Figure 1: Schematic diagram Power-to-Gas including reconversion into electrical power

Base is the presence of a well-developed natural gas infrastructure that is able to provide required capacities. Intention of Power-to-Gas is the transfer of electrical excess energy into chemical bond energy by electrolysis in the form of hydrogen. Hydrogen can be fed directly into the gas infrastructure in compliance with the limits of gas quality, furthermore, converted into methane by methanation. Among others, the total efficiency of the Power-to-Gas concept must be considered to evaluate the economy, including reconversion into electrical power and/or heat. A total efficiency of 30%, respectively 47% can be expected for combination of conventional low-temperature electrolysis with methanation including reconversion by *Combined Cycle Power Plant* (CCPP) or *Combined Heat and Power* (CHP). Higher efficiencies are met by using high-temperature electrolysis due to thermodynamic advantages.

2 High-temperature electrolysis and methanation

2.1. High-temperature electrolysis

The standard reaction enthalpy for water decomposition by electrolysis

$$H_2O_{(lq)} \rightarrow H_{2,g} + \tfrac{1}{2} O_{2,g} \qquad \Delta_R H^0 = 286 \text{ kJ/mol} \qquad (1)$$
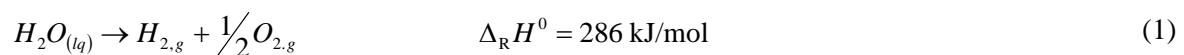
is supplied by electrical work. The equivalent potential difference corresponds to 1.48 V (standard conditions), according to

$$E_H^0 = -\frac{\Delta_R H^0}{z \cdot F}, \tag{2}$$

whereby $\Delta_R H^0$ is defined by

$$\Delta_R H^0 = \Delta_R G^0 + T \cdot \Delta_R S^0. \tag{3}$$

Only $\Delta_R G$ has to be added theoretically by electrical work. A Voltage of 1.23 V (standard conditions) is required, according to

$$E_G^0 = -\frac{\Delta_R G^0}{z \cdot F}. \tag{4}$$

The difference in form of $T \Delta_R S^0$ can be added by thermal energy. Liquid water is used for conventional low-temperature electrolysis (<100°C), hence enthalpy of vaporization must be delivered additionally, 0.23 V according to

$$U_V = \frac{\Delta H_V}{z \cdot F}. \tag{5}$$

$\Delta_R H$ und $\Delta_R G$ are functions of temperature, which also applies to the equivalent voltages (see figure 2).
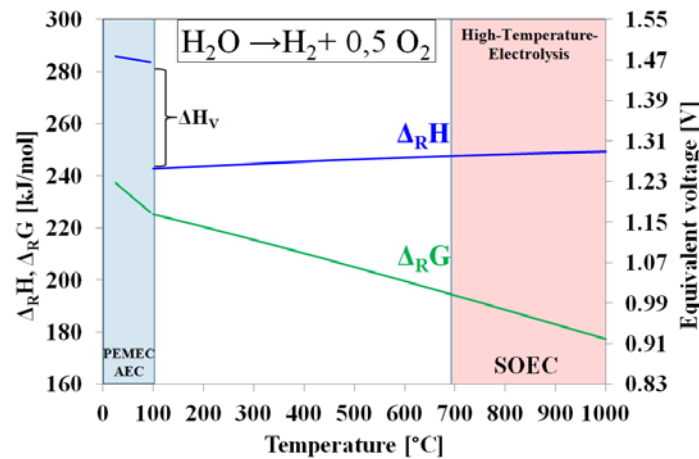
Figure 2: Reaction enthalpy $\Delta_R H$ & Gibbs enthalpy $\Delta_R G$ and equivalent voltage as function of temperature

The required minimum voltage can be reduced by the amount of voltage that corresponds to vaporization enthalpy in case of steam electrolysis. Furthermore, figure 2 shows clearly a decrease of ΔG with higher temperatures in contrast to ΔH. The higher the temperature the less is the required minimum voltage and thus the content of electrical work despite of necessary overvoltage for covering polarization resistance and ohmic losses. In this way, the high-temperature electrolysis contains energetic potential, especially in availability of waste heat from other processes. Three different operating modes exist, according to operating voltage:

- Endothermic operation: $U_B < E_H$

    The operating voltage U_B is less than the thermo-neutral potential difference E_H. Difference $(E_H - U_B)$ is supplied as thermal energy.

3

- Autothermal operation: $U_B = E_H$

  Operating voltage corresponds to the thermo-neutral potential difference. No thermal energy is delivered or required.

- Exothermic operation: $U_B > E_H$

  The operating voltage U_B is higher than the thermo-neutral potential difference E_H. Difference $(U_B - E_H)$ is delivered as thermal energy.

CO_2 can be also converted by high-temperature electrolysis in addition to H_2O, an interesting aspect in terms of measures for decreasing emissions of this greenhouse gas.

$$CO_2 \rightarrow CO + \frac{1}{2}O_2 \qquad \Delta_R H^0 = 283 \, kJ/mol \qquad (6)$$
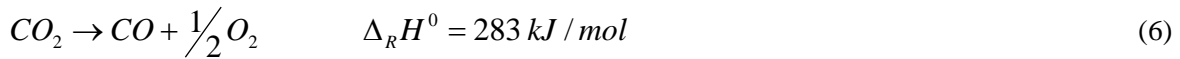
Furthermore, technical advantages are met. The product gas consists of H_2 and CO, typical components for syngas applications.

2.2 State of research in the field of high-temperature electrolysis

Alkaline electrolysis (AEC) on large scale and Proton-Exchange-Membrane electrolysis (PEMEC) on smaller scale are established than state of the art for low-temperature applications. R&D of high-temperature electrolysis is still in its infancy. One promising technology is the SOEC (Solid Oxide Electrolysis Cell). Activities in this field were started in the middle of the 1970s in Germany within the project HOT ELLY (High Operating Temperature Electrolysis) [2, 3]. However, intensive development efforts with the aim of maturity phase were not continued. Renewed activities were done in course of establishing high-temperature fuel cells based on solid oxide materials (SOFC) in the middle of the last decade. One reason is the reversibility of the process; cells based on SOFC can be used as SOEC after modifications of cell materials. Following reactions occur in the SOEC (figure 3):
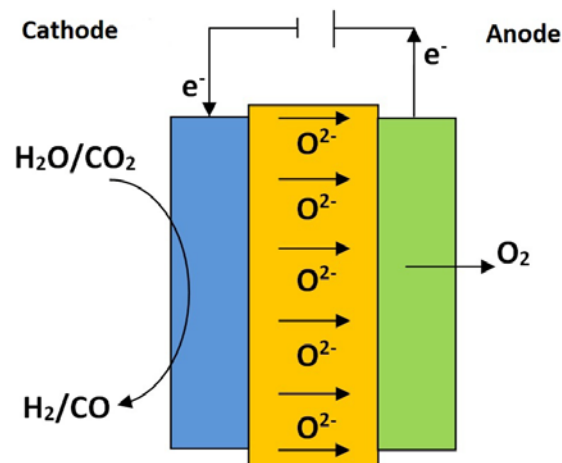

Figure 3: Principle of Solid Oxide Electrolysis Cell (SOEC)

Cathode reaction

$$2H_2O + 4e^- \rightarrow 2H_2 + 2O^{2-} \qquad\qquad 2CO_2 + 4e^- \rightarrow 2CO + 2O^{2-} \qquad (7)$$

Anode reaction

$$2O^{2-} \rightarrow O_2 + 4e^- \tag{8}$$

Global reaction

$$2H_2O \rightarrow 2H_2 + O_2 \qquad\qquad 2CO_2 \rightarrow 2CO + O_2 \tag{9}$$
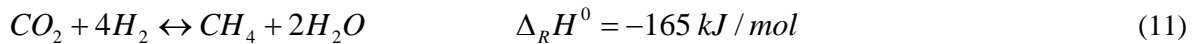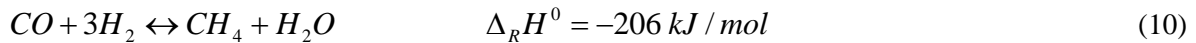
SOFC and SOEC consist of anode, cathode and electrolyte. Both are characterized by high electrode kinetics due to high operating temperatures, therefore no noble metal catalysts are needed. Yttrium-doped zirconia (YSZ) is the base material of the electrolyte, characterized by very good thermal stability and high ionic conductivity. In contrast to SOFC, SOEC exists only on laboratory scale. Development work will be carried out around the world, for example at the company *sunfire* in Germany [4], at *Topsoe Fuel Cell* and *Risø National Laboratory for Sustainable Energy*, *Technical University of Denmark* – DTU [5, 6], at *Idaho National Laboratory*, USA [7] and at the *Central Research Institute of Electric Power Industry*, Japan [8] to name only a few.

2.3 Methanation

Methanation describes the catalytic conversion of H_2 with CO or CO_2 into methane (SNG *Synthetic Natural Gas*) and water:

$$CO + 3H_2 \leftrightarrow CH_4 + H_2O \qquad\qquad \Delta_R H^0 = -206 \, kJ/mol \tag{10}$$

$$CO_2 + 4H_2 \leftrightarrow CH_4 + 2H_2O \qquad\qquad \Delta_R H^0 = -165 \, kJ/mol \tag{11}$$

Typical SNG-reactor concepts are fixed or fluidized bed reactors. Alternatively, there are investigations on using bubble column reactors, which offer advantages in the removal of reaction heat and temperature control [9]. Catalysts for methanation of CO and/or CO_2 are available on market; usually the methanation catalyst can be used for both. Results of own measurement data and published experimental [10, 11] data show higher conversion rates in case of CO-methanation (80-100%, 200°C) compared to CO_2 (40-90%, 250°C), particularly at lower temperatures. One reason is the thermodynamic stability of CO_2 compared to CO. Furthermore, CO_2-methanation can be described as combined reaction of water-gas-shift reaction and CO-methanation whereby the whole reaction proceeds more slowly. The reactions are mol-reducing and therefore favored by high pressures.

3. Procedural interconnections and potential of high-temperature electrolysis and methanation

3.1 Bases of calculation in *ASPEN PLUS®*

The fundamental aspect of interconnections that are shown in the following is given by the characteristic of different heat flows of the system. The summarized heat quantity generated by overvoltage (exothermic operation), cooling and the reaction heat of methanation is larger than the required heat quantity for vaporization and preheating of the reactant water in case of the following boundary conditions:

All determinations were carried out in *ASPEN PLUS*® using Gibbs-reactors and heat exchanger. A user model was implemented to calculate the electrolysis. Following parameters were set for simulation:

- Electrolysis conversion 80%

- Operation temperature high-temperature electrolysis 800°C

- Operation temperature low-temperature electrolysis 70°C

- Operation mode of high-temperature electrolysis is exothermic ($U_B = 1.4$ V; corresponds to an overvoltage of 0.11 V related to $E_{H,\,800°C}$)

- Operation mode of low-temperature electrolysis is exothermic ($U_B = 1.85$ V; corresponds to an overvoltage of 0.38 V related to $E_{H,\,70°C}$)

- Methanation 25 bar, 250°C

Waste heat from electrolysis was calculated according to

$$\dot{Q}_{Elyse} = \dot{H}_{H2O,in} + P_{el} - (\dot{H}_{H2O,out} + \dot{H}_{H2} + \dot{H}_{O2}) \tag{12}$$

$\dot{H}_{H2O,in}$ Supplied enthalpy flow of water

$\dot{H}_{H2O,out}$ Enthalpy flow of not converted water (20%)

$\dot{H}_{H2}, \dot{H}_{O2}$ Enthalpy flow of products

P_{el} Electrical power of electrolysis

with operating voltage U_B and current I_B

$$P_{el} = U_B \cdot I_B \tag{13}$$

whereby I_B is based on *2ⁿᵈ Faradays Law* and on converted water

$$I_B = \dot{n}_{H2O,u} \cdot z \cdot F \,. \tag{14}$$

A *Gibbs*-reactor was implemented for methanation. The calculated composition corresponds to the thermodynamic equilibrium that is based on given temperature and pressure.

Determination of efficiency was calculated on molar gross calorific value of methane (887 kJ/mol), according to:

$$\eta = \frac{\dot{n}_{CH4} \cdot H_{o,m}^0}{P_{el} + \dot{Q}_{VW,H2O} + \dot{Q}_{VW,CO2}} \tag{15}$$

$\dot{n}_{CH4}$ Methane product mole flow

$\dot{Q}_{VW,i}$ External heat flow for preheating educts to reaction temperature in case of reduced delivery of internal heat sources (H$_2$O → 800°C electrolysis, CO$_2$ → 250°C methanation)

Process simulations were done stationary without consideration of heat losses.

3.3 Procedural Interconnections

3.3.1 Low-temperature electrolysis including CO$_2$-methanation

Liquid water is fed into the exothermic operating electrolysis in low-temperature region; the enthalpy of vaporization must be applied additionally in the form of electric energy.
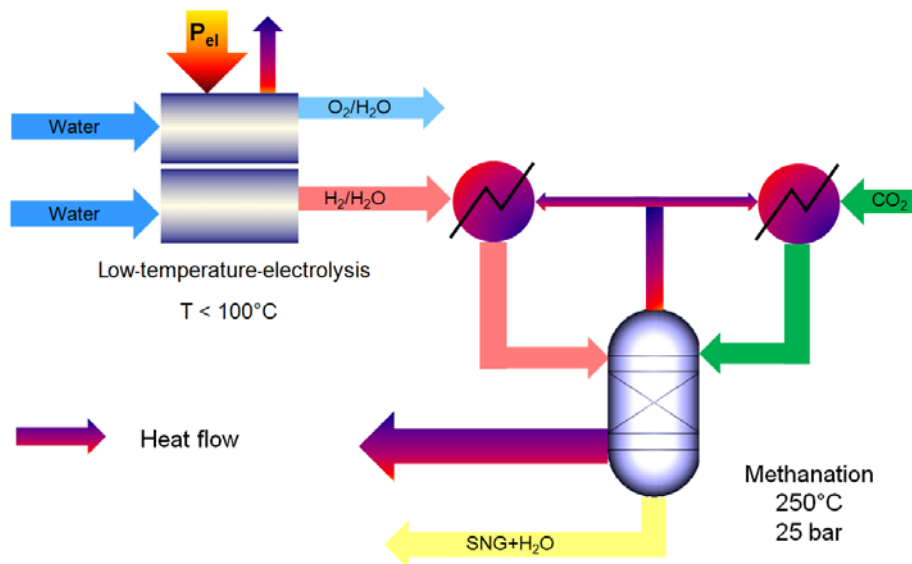
Figure 4: Low-temperature electrolysis coupled with CO$_2$-methanation

Figure 4 demonstrates the interconnection schematically with the example of alkaline electrolysis. Reaction heat of methanation was used as heat source and cold educt streams of electrolysis (H$_2$, CO$_2$) as heat sink respectively. The electrolysis waste heat at low temperature level is not included. The total efficiency of the system is 61%. If H$_2$ is considered as the target product without methanation a total efficiency of 80% is achieved.

3.3.2 High-temperature electrolysis including methanation

The combination of high-temperature electrolysis and CO$_2$-methanation offers opportunities in heat recirculation due to additional heat sources and sinks. This refers to methanation reaction heat as well as cooling of product stream after methanation in addition to the electrolysis and product streams waste heat (figure 5). Exothermic methanation reaction heat is integrated completely into the vaporization of process water. A total efficiency of 81% was determined for this kind of interconnection in exothermic operation of electrolysis.
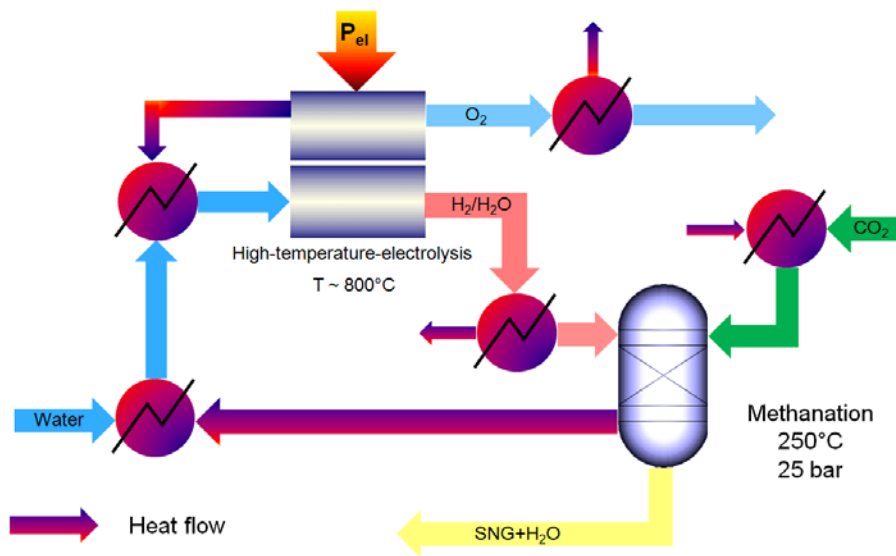
Figure 5: How-temperature electrolysis coupled with CO₂-methanation

3.3.3 High-temperature co-electrolysis including CO-methanation

High-temperature electrolysis offers the opportunity to convert CO_2 electrochemically into CO and O_2 in addition to the conversion of steam at a high temperature level. Steam and CO_2 are preheated together to the temperature level of electrolysis (figure 6). H_2O/CO_2-ratio of 3.0 describes the stoichiometry of the following CO-methanation. A total efficiency of 82% was determined for this kind of interconnection in exothermic operation of electrolysis. Noticeable in this interconnection is a higher heat output in methanation. The electrolysis product gas contains CO primarily in addition to H_2; it follows a higher heat extraction due to higher methanation reaction enthalpy of CO compared to CO_2-methanation (according to equations 10, 11).
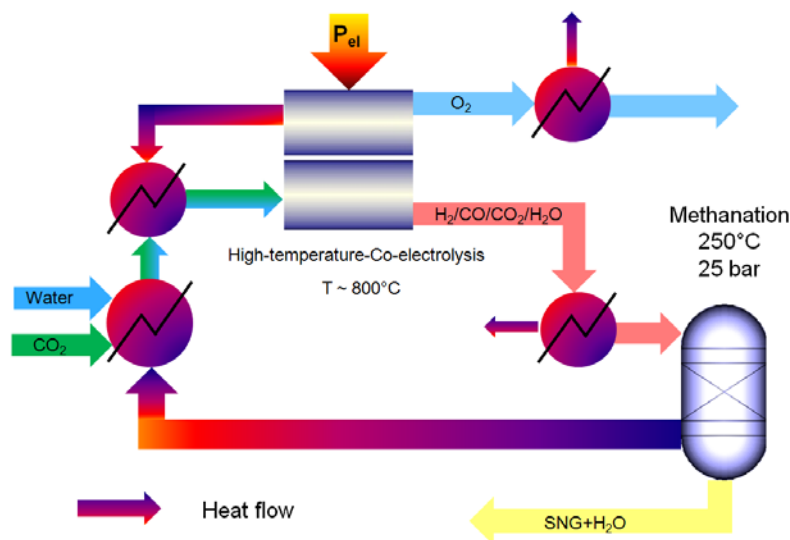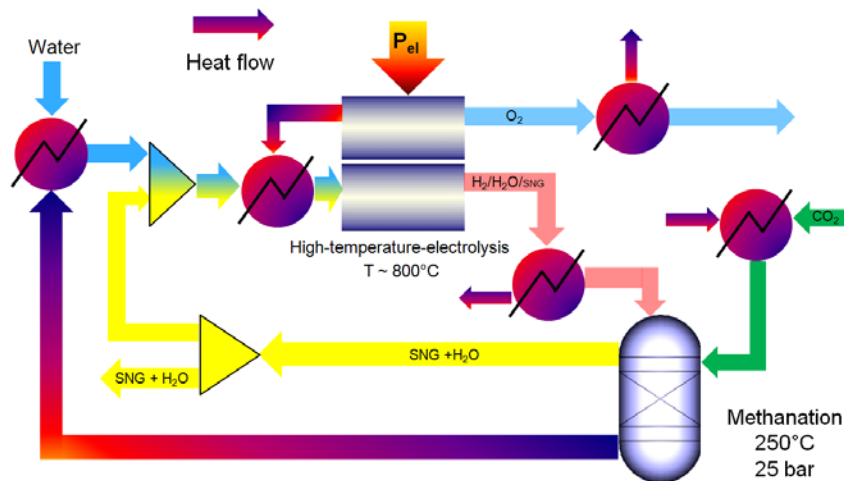

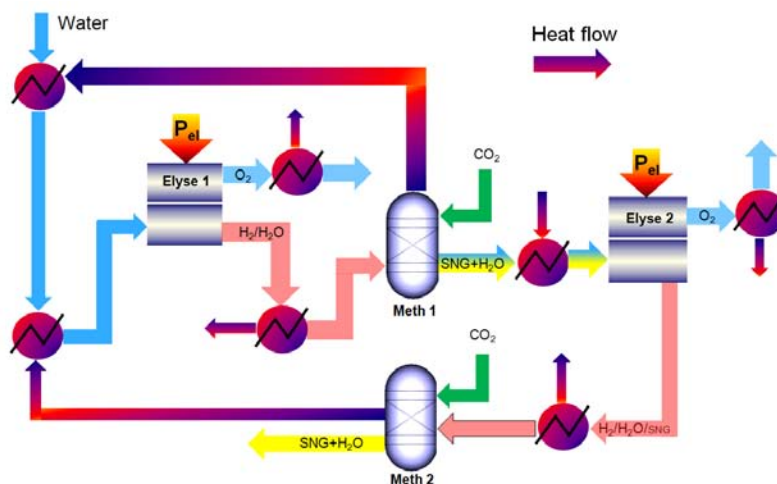**Figure 6: High-temperature co-electrolysis with CO-methanation**

3.3.4 High-temperature electrolysis including methanation and recirculation

Figure 7: High-temperature electrolysis with CO₂-methanation and recirculation

According to equation (11) water is the primary product component of CO_2-methanation in addition to CH_4 ($CH_4/H_2O=1/2$). The condensing of water content leads to loss of vaporization enthalpy. A fraction of methanation product stream is recirculated into the high-temperature electrolysis. Steam demand of the whole system including required preheating heat demand is minimized by this measure (figure 7). Fundamental requirement is no catalytic activity in terms of chemical reactions like water-gas-shift and steam reforming in addition to the electrochemical conversion. A total efficiency of 81% was determined for this kind of interconnection in exothermic operation of electrolysis.

3.3.5 High-temperature electrolysis including CO₂-methanation in cascades

**Figure 8: High-temperature electrolysis with CO₂-methanation in cascades**

Steam that is generated in methanation is used in a following process step in analogy to interconnection including recirculation. In contrast to recirculation this is realized by coupling of a further high-temperature electrolysis-methanation-module (figure 8). No other chemical reactions take place within electrolysis like in the variant of recirculation. In principle, several modules can be coupled. However,

amount of steam decreases from step to step and following modules are smaller in performance. Furthermore, increase of CH_4-content is limited by thermodynamic equilibrium. A total efficiency of 88% was determined for this kind of interconnection. The high efficiency is explained as following: Reaction heat of exothermic operating methanation cannot cover completely required vaporization enthalpy of process water. However, in case of coupling the first set up of electrolysis and methanation with methanation of second module required vaporization enthalpy is covered. Furthermore, steam can be preheated up to 240°C. Total efficiency decreases if a third module is coupled because no suitable heat sink exists for reaction heat of the third methanation step.

3.3.6 Discussion

The calculations have shown that high efficiencies are achieved by coupling high-temperature electrolysis and methanation. Independent of interconnection the maximum efficiency is given in endothermic operation of electrolysis. In this operational mode the difference between operating voltage and thermo-neutral voltage is covered by external heat supply resulting in a constant efficiency for endothermic operation independent of amount of voltage (valid for $U_B \leq$ x $\leq U_H$). Furthermore, as long as resulting waste heat can be integrated into preheating of educt streams efficiency is not decreased with exceeding the thermo-neutral voltage into exothermic operation. Efficiency begins to decrease if this demand is covered because no suitable heat sink exists. Interconnection containing cascades is characterized by highest total efficiency. However, determinations must be carried out in terms of technical feasibility due to unwanted side reactions like water-gas-shift and steam reforming at cathode side of electrolysis. Furthermore, real efficiency is decreased by heat losses.

4. Summary
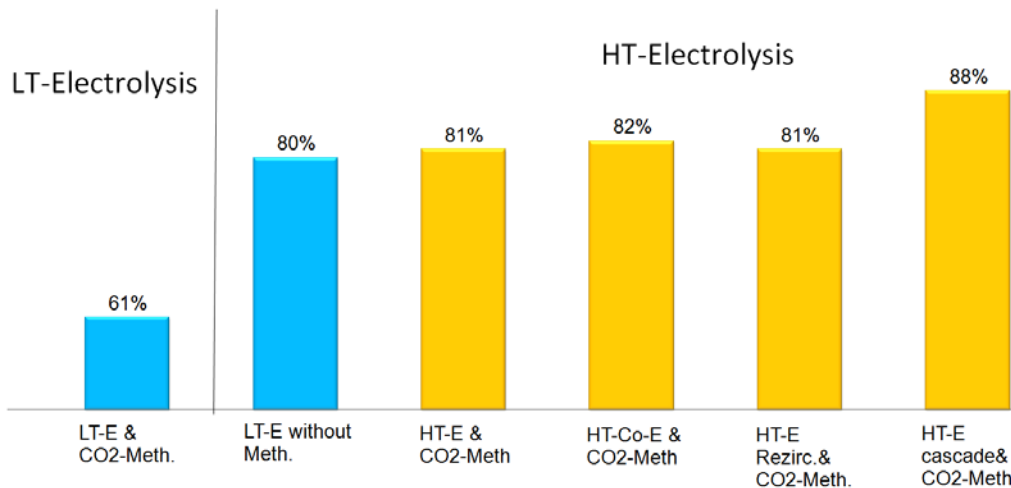
Figure 9: Summary, total efficiency of investigated interconnections

The system efficiencies of investigated interconnections are summarized in figure 9. The potential of increase in efficiency (>20%-points) by coupling high-temperature electrolysis with methanation compared to the low-temperature electrolysis-system can be seen clearly. Figure 10 illustrates individual efficiencies in the process chains of both variants including reconversion into electrical power and/or heat. For example, the total efficiency of process chain related to Combined Heat and Power

(CHP) can be increased from 47.3% to 68.4% by using interconnection variant of high-temperature electrolysis in cascades. Development in field of high-temperature electrolysis based on SOEC is at an early stage. However, there are international efforts to raise the technology from laboratory scale to higher level. Potential shows that by reaching technical maturity an efficient method is given to store volatile renewable energies.
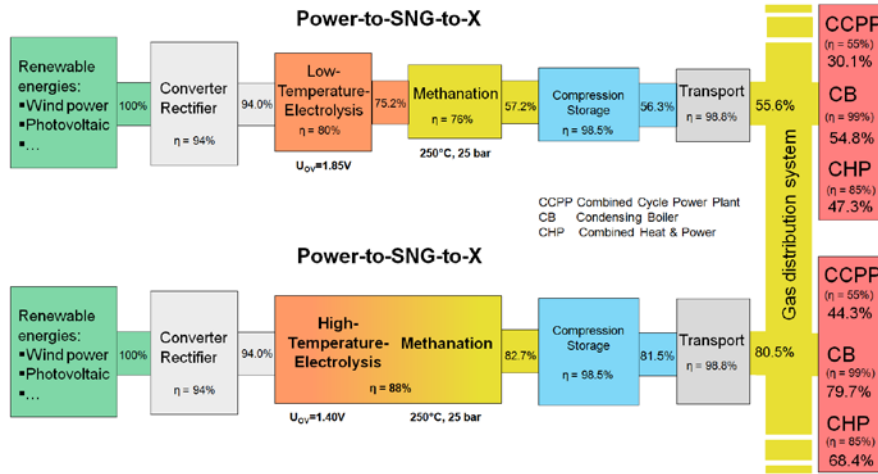
Figure 10: Comparison low- and high-temperature interconnections coupled with methanation, individual efficiencies and total efficiency including reconversion into electrical and/or thermal energy

Formula symbols

E^0_H	Thermo-neutral potential difference
E^0_G	Equivalent potential difference related to free standard reaction enthalpy
F	Faraday's constant (96485 C/mol)
$\Delta_R G^0$	Free standard reaction enthalpy (298 K, 1 atm)
$\Delta_R H^0$	Standard reaction enthalpy (298 K, 1 atm)
$H^0_{o,m}$	Molar gross caloric value methane (887 kJ/mol)
ΔH_V	Vaporization enthalpy
I_B	Operating current
$\dot{n}_{H2O,u}$	Mole flow converted water (electrolysis)
$\dot{n}_{CH4}$	Mole flow methane
P_{el}	Electrical power
$\Delta_R S^0$	Standard reaction entropy (298 K, 1 atm)
U_B	Operating voltage
z	Valence = 2 (electrolysis reaction H_2O, CO_2)

Abbreviations

AEC	Alkali Electrolysis Cell
CB	Condensing Boiler
CCPP	Combined Cycle Power Plant
HOT ELLY	High Operating Temperature Electrolysis
HT	High-temperature
CHP	Combined Heat and Power
LT	Low-temperature
PtG	Power-to-Gas
PEMEC	Proton-Exchange-Membrane Electrolysis Cell
PV	Photovoltaic
SNG	Synthetic Natural Gas
SOEC	Solid Oxide Electrolysis Cell
SOFC	Solid Oxide Fuel Cell

Literature sources

[1]   Eurostat: Anteil erneuerbarer Energien stieg auf 13% des Energieverbrauchs in der EU27 im Jahr 2011, eurostat press release, STAT/13/65, http://ec.europa.eu/eurostat/, 2013

[2]   Quandt, K.H.; Streicher, R.: Concept and design of a 3.5 MW pilot plant for high temperature electrolysis of water vapor, International Journal of Hydrogen Energy, Vol. 11, No. 5, pages 309-315, 1986

[3]   Doenitz, W.; Erdle, E.: High-temperature electrolysis of water vapor—status of development and perspectives for application, International Journal of Hydrogen Energy, Vol. 10, No. 5, pages 291-295, 1985

[4]   Funding project "Sunfire", sponsored by Federal Ministry of Education and Research, Germany, http://www.sunfire.de/produkte/fuel/power-to-liquids, 1.8.2014

[5]   Chen, M., et al.: High-Temperature Co-Electrolysis of Steam and CO_2 in an SOC Stack: Performance and Durability, Fuel Cells, Special Issue: 10th European SOFC Forum (EFCF 2012) Volume 13, Issue 4, pages 638-645, 2013

[6]   Ebbesen, S.D., et al.: Durable SOC stacks for productionof hydrogen and synthesis gas by high temperature electrolysis, International Journal of Hydrogen Energy, Vol. 36, No. 13, pages 7363-7373, 2011

[7]   O'Brien, J.E.; et al: Parametric study of large-scale production of Syngas via high-temperature co-electrolysis, International Journal of Hydrogen Energy, Vol. 34, pages 4216-4226, 2009

[8]   Wang, Z.; et al.: Steam electrolysis performance of intermediate-temperature solide oxide electrolysis cell and efficiency of hydrogen production system at 300 Nm³ h-1, International Journal of Hydrogen Energy, Vol. 35, pages 4451-4458, 2010

[9]   Götz, M., et al.: Einsatz eines Blasensäulenreaktors zur Methansynthese, Chemie Ingenieur Technik, Volume 85, Issue 7, pages 1146-1151, 2013

[10]   Kustov, A. L., et al.: CO Methanation over supported bimetallic Ni-Fe catalysts: From computational studies towards catalyst optimization, Applied Catalysis A: General 320, Pages 98-104, 2007

[11]   Schoder, M., et al.: Heterogen katalysierte Hydrierung von Kohlendioxid zu Methan unter erhöhten Drücken, Chemie Ingenieur Technik 85, Nr. 3, Seiten 344-352, 2013